CREOSOTE: REVIEW OF WORKER EXPOSURE STUDY

1.0 INTRODUCTION

The purpose of this report is to review the worker exposure study submitted to the U.S. Environmental Protection Agency in support of the re-registration requirements of the wood preservative, creosote. The creosote worker exposure study was submitted to fulfill agency guideline requirements under Series 875.1100 Dermal Exposure- Outdoor [1]; Series 875.1300 Inhalation Exposure- Outdoor [2]; and Series 875-Occupational and Residential Exposure Test Guidelines, Group B Post application Exposure Monitoring Test Guidelines [3]. The major points in "Checklist for Applicator Monitoring Data" were used to evaluate compliance with Series 875.

The following information can be used to identify the protocol:

Title	Formulation, Active Ingredient	Identifying Codes	Corporate Sponsor	Performing Laboratory
Assessment of Potential Creosote Inhalation and Dermal Exposure Associated with Pressure-Treatment of Wood with Creosote	(1)Koppers Coal Tar Creosote with 98.5% active ingredient (a.i.) creosote (AWPA P1/P13) (2) VFT Coal Tar Creosote Wood Preservative with 100 % a.i. creosote (P1/P13) (3) Koppers Creosote Solution with 95% a.i. creosote (AWPA P2)	MRID No. 453234-01; AASI Study No. AA990308; EN-CAS Analytical Laboratories Project No. 98-0079	Creosote Council II John H. Butala, DABT 7 Glasgow Road Gibsonia, PA 15044 Phone: (724) 443-0097 FAX: (724) 443-0926	Field Mark G. Bookbinder (Field Investigator) c/o American Agricultural Services, Inc. 404 E. Chatham Street Cary, NC 27511 Phone/FAX: (301) 540-5622 Analytical Bert Clayton, B.S. (Dermal Exposure Support) EN-CAS Laboratories ("ENCAS") 2359 Farrington Point Drive Winston-Salem, NC 27107 Phone: (336) 785-3252 FAX: (336) 785-3262 Stephanie Guilyard (Inhalation Exposure Support) USX Engineers and Consultants, Inc. (UEC) 4000 Tech Ctr. Dr. Monroeville, PA 15146 Phone: (412) 825-2808 FAX: (412) 825-2022

2.0 EXECUTIVE SUMMARY

This study was designed to estimate the exposure to creosote of individuals performing job functions involved in commercial pressure treatment of lumber, utility poles, and railroad ties at four typical commercial treatment facilities in the United States and Canada (referred to as Sites A through D). Three end use products for coal tar creosote were used. Twenty-five workers and 11 job functions (tasks) were monitored for up to 4 or 5 consecutive work days each (8 hour shifts). Many of the job functions may have been performed by one or more worker(s). Where a single worker performed the duties of more than one job function, the title of the job function which represented the majority of their work efforts was used to identify the worker.

Dermal and inhalation exposure levels were estimated. Dermal exposure levels were estimated by passive dosimetry using whole body dosimeters (WBDs) and cloth dosimeter gloves. The WBDs and cloth dosimeter gloves were worn under the workers' protective clothing and chemical resistant gloves. Inhalation exposure levels were estimated by active dosimetry using a sampling train (placed in the worker's breathing zone) that consisted of a PTFE air filter upstream from two in-line XAD-2 resin filled air sampling tubes. The air was pulled through the sampling train by a portable air sampling pump.

Creosote cannot be measured directly because it is a mixture of many component compounds. Dermal exposure to "total creosote" was estimated by measuring the levels of ten individual polynuclear aromatic hydrocarbon (PNA) compounds. Each analyte was determined in each WBD and glove sample as if it represented total creosote. Inhalation exposure was estimated for 11 individual PNA compounds as well as for benzene-soluble PNAs and related compounds collectively known as coal tar pitch volatiles (CTPVs). The PTFE filter retained the CTPVs, while the PNAs were retained in the XAD-2 resin tubes.

Known quantities of a characterized creosote formulation could not be measured because the study was set up in a continuously operating commercial setting. The creosote was applied in closed systems where excess treatment solution from the wood and treatment vessels were recovered and retained while sealed. Therefore, the amount of product or active ingredient handled by each worker is not known. According to the Study Report, the major source of creosote for worker exposure in this type of facility is due to preservative remaining on or escaping from treated wood or equipment that had been in a cylinder during treatment. This is presumably a very small fraction of the quantity actually applied to and retained by the charge. The treated wood retained between approximately 5794 pounds (Site B) and 53290 pounds (Site C) of creosote per charge, depending on treatment parameters. This study monitored 12 (Site A) to 23 (Site D) charges.

The unadjusted creosote level for each WBD segment and glove pair from each worker was corrected for the mean field fortification recovery of the appropriate analytical standard(s) from samples fortified in the field at that test site. The analytical method was subject to some variability at levels near the LOQ, suggesting that recoveries obtained at that level were likely to be less reliable than those at the higher level. Therefore, the field fortification recoveries at 1,000 times the LOQ were used to make the corrections. The registrant did not make corrections to the raw data when field fortification recoveries were > 100%. U.S. EPA guidelines state that corrections are not needed when field fortification recoveries are above 90%.

Each calculated exposure level was normalized to μg/kg body weight/day, normalizing results to the EPA recommended mean adult weight of 71.8 kg and to a standard work day length of 8 hours. The "total" dermal exposure for each replicate for each worker was calculated by summing the normalized residue levels in the WBD arms, WBD top, WBD bottom (torso portion and legs, cut apart at EN-CAS and analyzed as separate samples), and all glove dosimeters worn during that replicate. Geometric mean dermal creosote exposures across all of the job functions at all four sites ranged from 25 (Load-Out Area Helper) to 901 (Oil Unloader) μg/kg bw/day.

The highest individual levels were found for the Site C Treatment Operator. This operator also performed the duties of the Oil Unloader while not wearing chemical-resistant gloves on at least one monitored occasion. Within each job class monitored, and over all classes at each site, those individuals whose activities involved the greatest proximity to creosote sources were exposed to the highest levels of creosote.

No useful inhalation data were generated at Site A due to problems with the air sampling methodology. The methodology was changed prior to sampling at Sites B, C, and D (added second XAD-2 resin tube to sampling train). The unadjusted inhalation residue level for each air sampler from each worker was corrected for the mean field fortification recovery of the appropriate analytical standard(s) from samples fortified in the field at that test site. Calculated inhalation exposure levels were normalized by scaling up the pump flow rate of 1 L/min to the EPA recommended minute ventilation rate of 1100 L/hr (approximately 18.34 L/min) for "light activities", and then adjusting for the standard EPA-recommended adult weight of 71.8 kg.

Chrysene and benzo(a)pyrene were not detected in worker samplers. Pyrene and anthracene were detected in 1 and 2 sampler(s), respectively. However, naphthalene was detected in every sampler, and 2-methylnaphthalene was detected in most samplers, suggesting that only the lower molecular weight ("low-boiling") PNAs are commonly volatilized during pressure treatment, or are able to remain volatile when exposed to ambient temperatures. Naphthalene represented the single greatest contribution to inhalation exposure. CTPVs were present at quantifiable levels in only one sampler, suggesting that this class of compounds may be a minor constituent of creosote emissions. Measured aerial concentrations of naphthalene (approximately 0.04 to 1.29 mg/m^3) and CTPVs (0.0003 to 0.0006 mg/m^3) were well below the ACHIH TLVs of 52 mg/m^3 and 0.2 mg/m^3, respectively, for these materials for all monitored workers. The geometric mean daily inhalation exposure was greatest in worker classes performing tasks in close proximity to sources of creosote.

The concerns related to requirements under the Series 875 guidelines are as follows:

(1) CTPV inhalation field fortification recoveries and some dermal field fortification recoveries were unacceptable;

(2) Unable to quantitate the total amount of active ingredient handled by each worker monitored in the study;

(3) There were not enough field fortification samples and field blanks collected; and

(4) The amount of product applied was not measured.

The study did address most of the issues in Series 875 (the method validation, field spikes, and QA/QC were more thorough then most studies), but the poor recoveries were major issues that did not meet Series 875 guidelines. The calculation of inhalation exposure results was not described well. The raw data supplied in the study did not directly match up with the bar graphs presented.

3.0 BACKGROUND

3.1 Introduction

Four commercial facilities in the U.S. and Canada were used in this study to determine the dermal and inhalation exposure of workers applying creosote end use products to wood poles and/or railroad ties by pressure treatment systems. Three of the facilities (referred to herein as Sites A, C, and D) were located in the U.S. (Florence, South Carolina; Denver, Colorado; and Somerville, Texas). The fourth facility (referred to herein as Site B) was located in Delson, Quebec, Canada. The four facilities and the end use products used in this study were said to represent a range of geographic locations, formulations used, species of wood products treated, and application parameters used for treatment of wood with creosote.

At each site, pressure treatment of wood products was performed using the same basic process. Workers operating self-propelled or stationary loaders moved untreated poles or ties from holding areas and stacked them onto wheeled metal trams on a railroad track leading into the treatment cylinder(s). When enough trams were loaded to fill a cylinder, the poles or ties on each tram were tied together with chains of metal or plastic bands. A charge cable (or "lead cable") was connected to the tram farthest from the cylinder door, and laid along the top of the stacked items on the trams. The filled trams were considered a "charge" of wood products.

The cylinder door was opened and its drawbridge was positioned so that it connected the drip pad track with the cylinder's interior rails. The charge was then pushed into the cylinder by a self-propelled loader. Workers placed the free end of the lead cable into the cylinder, closed the cylinder door(s), and started the treatment process. Treating solution (P1 or P2, as unloaded from tank cars in which it was delivered to the plant) was heated to 190 - 210 ^{o}F and pumped from storage tanks into the cylinder, after which pressure (150 - 190 psi) was applied to the cylinder to allow the preservative to permeate the wood of the poles.

After treatment, excess treating solution was removed from the cylinders and wood products by maintaining a vacuum in the cylinder for approximately 1 to 7 hours. The duration of a treatment cycle ranged from approximately 7 to 80 hours, depending on the species of wood treated and the procedures used by each site. At the end of treatment, the cylinder was opened, and excess water and creosote vapors and condensates evolved from the cooling wood products (charges typically generated condensate plumes for up to several hours after treatment).

Workers removed the charge from the cylinder by removing the end of the lead cable from the cylinder and attached it to a hook on a self-propelled loader, which then pulled the loaded trams out of the cylinder. At Sites A, B, and C, each charge was pulled onto a concrete "drip pad," where excess treatment solution was allowed to drip from the wood products and trams onto the pad for up to several hours. After site personnel removed lead cables and chains, the cooled poles were pushed by loader to a storage area, where workers using hand- or electric-powered drills took narrow cores of wood from selected poles or ties to determine the depth of

penetration of the preservative, and the amount of preservative that actually was absorbed by the wood. Charges that did not contain enough creosote or did not penetrate deep enough were retreated as above. At Site D, ties were pushed down the length of the drip pad to more distant areas of the plant for stacking. The ties were immediately transfered to rail cars following their withdrawal from the cylinder. Test boring was not routinely performed at this site, per customer specifications.

Twenty-five workers were monitored for this study. The 11 treatment plant job categories monitored in this study include treatment operators, treating assistants, loader operators (cylinder and load-out areas), cylinder-area helpers, checker, load-out area helpers, test borers, oil unloaders, drip pad laborer and water treatment system operators. Workers performed typical tasks related to these activities and were monitored for up to 4-5 consecutive work days each. Descriptions of the tasks monitored are bulleted below :

- **Treatment operators (TOs)** - TOs operated and monitored application system valves and controls, they sometimes opened and closed cylinder doors, and they supervised the insertion and removal of charges (loads of dried, debarked poles or untreated ties) of poles from the treatment cylinders.

- **Treating assistant (TA)** - TAs performed many of the same functions as the TOs and sometimes assisted the TO in charge preparation, cylinder cleaning and maintenance, filter cleaning, mixing of treatment solution, and also participated in some loader operations moving charges.

- **Loader operators (CLOs in the cylinder area, and LLOs in the load-out areas)** - LOs stacked untreated wood onto charge trams, moved charges into and out of treatment cylinders, distributed treated wood to load-out area, and loaded treated wood for shipment.

- **Cylinder-area helpers (CHs in the cylinder area, and LHs in the load-out areas)** - CHs/LHs aided the LOs by opening/closing cylinder door, cleaning door debris and performing door maintenance, handling charge leads and cables, and banding stacked wood.

- **Checker (CK)** - CKs performed many of the duties of a CH.

- **Load-out area helpers (LHs)** - LHs aided their LOs by banding treated wood and removing culls.

- **Test borers (TBs)** - TBs took cores from freshly treated poles or ties to be tested for creosote content and penetration depth.

- **Oil unloaders (OUs)** - OUs operated the equipment that transferred creosote from rail tank cars to treating system tanks.

- **Drip pad laborer (DP)_**- DPs steam-cleaned drip pads and tracks. They also picked up and disposed of treated wood waste and performed various labor clean-up duties in treatment areas.

- **Water treatment system operators (WOs)** - WOs controlled equipment that collected drip-pad effluent water, and removed creosote and other contaminants.

Creosote is a complex mixture of chemicals and therefore can not be measured directly. Dermal exposure levels were estimated by passive dosimetry using whole body dosimeters (WBD) which were worn under the worker's clothing and lightweight cotton glove dosimeters which were worn under work gloves. The dermal creosote exposure levels were estimated by measuring the levels of ten individual polynuclear aromatic hydrocarbon (PNA) compounds. Each of these analytes were determined in each WBD and glove sample as if it represented total creosote. The levels for each of the individual analytes were then averaged together to estimate the level of total creosote present in/on the individual sample.

Inhalation exposures for each worker was estimated by active dosimetry. Each worker wore a sampling train consisting of a PTFE filter upstream from two in-line XAD-2 resin-filled air sampling tubes. The inhalation exposure levels were estimated by determining the presence of specific individual creosote components (11 individual PNAs representing the boiling point ranges of known creosote components). Inhalation exposure to benzene-soluble PNAs and related components collectively known as coal tar pitch volatiles (CTPVs) were measured as well. The PTFE filter retained the CTPVs, while the PNAs were retained in the XAD-2 resin tubes. A more complete description of the monitoring techniques used in this study is described in Section 5.

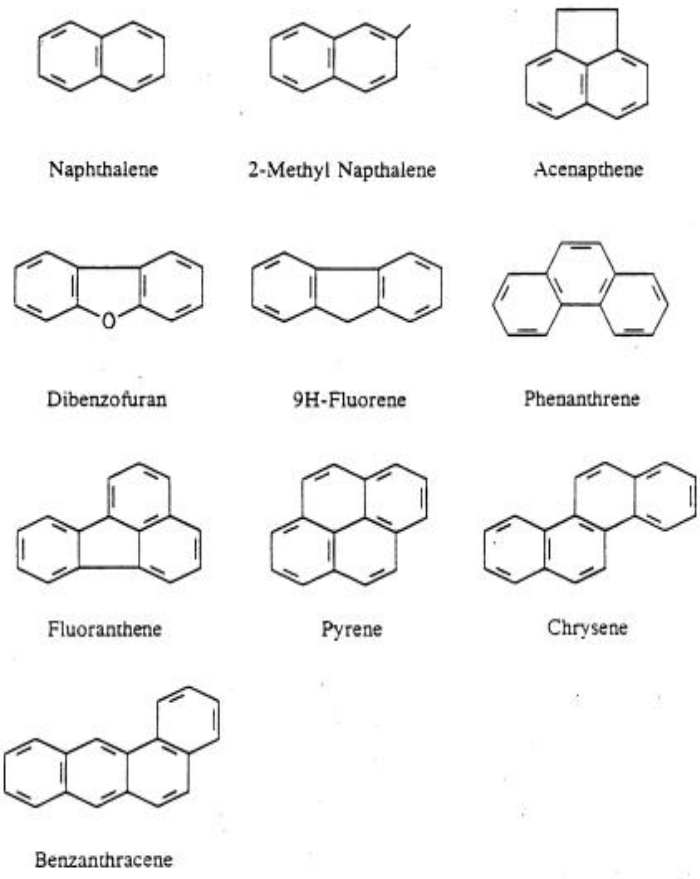
3.2 Physical and Chemical Characteristics of Creosote

Coal-tar creosote is a blend of over 200 compounds, and approximately 85% of it is composed of polynuclear aromatic hydrocarbons (PNAs). Some of the more significant compounds in creosote are: naphthalene, acenaphthene, fluorene, phenanthrene, fluoranthene, and pyrenes.[4] Vapor pressures for naphthalene, phenanthrene, pyrene, and chrysene are 8.7E-02, 9.6E-04, 6.8E-07, 6.3E-09 mm Hg respectively.[5] The volatiles are the single ring compounds and the semi-volatiles are the two to six ring compounds.[6] The vapor pressure tends to become larger as aromatic rings are added to the compound. The more soluble compounds of creosote include phenols, cresols, and N-heterocyclics. PNA compounds have various physical and chemical characteristics. The lower molecular weight PNAs are more biodegradable, volatile, and water-soluble than the heavier compounds. PNAs are biodegradable, especially under aerobic conditions (in the presence of oxygen). The high molecular weight PNAs tend to have low aqueous solubilities. Several of the lower molecular-weight PNAs are also biodegradable under anaerobic conditions (in the lack of oxygen).

3.3 Chemical Structure, Fate, and Dissipation

Chemical Name: Creosote
CAS: 8001-58-9
Structures for creosote are presented below.

The following are the structures of the marker compounds.



The compounds with the higher molecular weights tend to be more persistent. Water solubility, and thus bio-availability has been found to be inversely proportional to the size of the molecule. PAHs with two rings, generally have half lives less than 10 days. Three ring PAHs generally exhibit longer half lives in most cases, but these compounds have half lives of less than 100 days. Four or five ring PAHs have half lives from 100 days or more. However, under certain conditions this group has exhibited half lives under 10 days.[6]

4.0 PURPOSE

This study was conducted to estimate the exposure to creosote of individuals performing routine tasks involved in the commercial pressure treatment of lumber, utility poles, and railroad ties at four typical commercial treatment facilities in the U.S. and Canada, per the requirements of the U.S. Environmental Protection Agency, California Department of Pesticide Regulation, and Health Canada's Pesticide Management Regulatory Authority regulations. Dermal and inhalation exposure monitoring data were gathered for each job function of interest. This study review will provide a summary of the procedures used in the study, results obtained by the study, a review based on Series 875 guidelines, and a conclusion indicating identified gaps.

5.0 PROCEDURE

5.1 Mixing/Loading/Application Method

The procedures used for mixing and loading the product were not discussed in detail in the study. The study reported that the treating solution (P1 or P2) was unloaded from tank cars in which it was delivered to the plant and was heated to 190 - 210 ^{o}F and pumped from storage tanks into the cylinder, after which pressure (150 - 190 psi) was applied to the cylinder to allow the preservative to permeate the wood of the poles.

Known quantities of the creosote formulations used at each of the sites were not measurable for this study because the study was set up in continuously operating commercial settings. The creosote was applied in closed systems which recovered and retained excess treatment solution from the wood and treatment vessels while sealed. Therefore, the amount of product or active ingredient handled by each worker is not known.

5.2. Exposure Monitoring

Dermal

The creosote dermal exposure to each worker was determined using a whole-body dosimeter (WBD), consisting of a 100% cotton thermal shirt and long pants. Each worker at Sites A, C, or D wore his WBD under a fresh work uniform consisting of a cotton long-sleeved work shirt and cotton work trousers (or one-piece cotton coverall) provided by the test site. The workers at Site B were not provided uniforms therefore, for the purpose of this study, each worker wore a WBD under a fresh lightweight cotton/polyester sweat shirt and pants purchased locally by study personnel. Each worker at all four sites wore a lightweight 100% cotton glove dosimeter on each hand , under his chemical-resistant or work gloves as appropriate.

At the beginning of each work cycle (or 8 hour shift), each worker washed his hands with a detergent and then put on his WBD, followed by his fresh uniform and other work clothes.

Once the worker was ready to start his work cycle, study personnel placed his glove dosimeters on his hands. At each rest or other break, study personnel removed the worker's glove dosimeters, wrapped the pair in aluminum foil (except for certain samples from Sites A and B), placed them in a locking polyethylene storage bag and froze them on dry ice. When the break ended, the worker put on a fresh pair of glove dosimeters. At the end of the work day, study personnel collected the worker's glove dosimeters and handled them as noted above. The study personnel helped each worker remove his outer work clothes and then cut the WBD from him in sections, including paired arms, remainder of shirt ("torso top"), briefs and paired legs. Each section was packaged as described above, labeled, and placed on dry ice for shipment to EN-CAS Laboratories.

Inhalation

Inhalation exposure monitoring at Site A was unsuccessful due to fact that a single XAD-2 tube was used along with a non-solvent-resistant filter cassette. Therefore, the sampling methodology was changed to include the use of a second XAD-2 resin tube in the sampling train prior to sampling at Sites B, C, and D. Inhalation exposure monitoring was performed successfully at these sites. Each worker at Sites B, C, and D was equipped with an air sampling train consisting of a PTFE filter in an opaque, solvent-resistant plastic cassette connected upstream from two in-line XAD-2 resin-filled air sampling tubes. The intake orifice of the filter was placed in the worker's breathing zone, directed downward. Air was pulled through the sampling train by a portable air sampling pump which was attached to the worker's belt. The pump drew air through the sampling tube at approximately 1 L/minute while the worker performed his tasks. Pumps were calibrated immediately prior to and after each monitoring period using a mass flow meter or bubble calibrator. The pumps were turned on at the beginning of each work cycle and was left running during restroom, coffee, or other short breaks but were turned off or set on "hold" during lunch breaks. The pumps and samplers were removed from the worker during the lunch break. At the conclusion of the lunch break, the pump and sampling train were reinstalled and the pump was restarted. All start and stop times were recorded.

During each work cycle, start times and end times of each task performed by the worker were recorded. Pump parameters during use were also recorded. At the end of each work cycle, the pumps and sample trains were collected. Each filter cassette and sampling tube were capped, labeled, bagged, and placed on dry ice for shipment to USX Engineers and Consultants, Inc. (UEC) for extraction and analysis. After the collection of the air samples the air sampling pump was re-calibrated.

5.3 Analytical Methods

Dermal

Residues of creosote components in dermal exposure monitoring matrices were

determined by the validated EN-CAS Method ENC-2/99, dated 04/18/00. For this procedure, a dermal sample is placed into glass jar (size of jar is dependant upon the size of the sample). The dermal sample consists of either (1) one brief with the elastic waistband removed or (2) two leg sections cut off at the crotch, or (3) two arm sections, or (4) one torso section or (5) two glove liners.

An appropriate amount (depending on the type of dermal sample) of 90:10 acetonitrile (ACN):dichloromethane (DCM) extraction solvent was added to the jar. The jar was then capped and shaken for 30 minutes at 250 rpm. An aliquot of the extract was mixed with de-ionized water, saturated NaCl solution, and hexane in a separatory funnel. The mixture was shaken vigorously for approximately 30 seconds, and the layers were allowed to separate for 5-10 minutes. The organic layer from the separatory funnel was passed through a rinsed Na_2SO_4 powder funnel, containing a glass wool plug, into a clean glass flask. The aqueous layer was partitioned a second time with hexane. The hexane layer was drained through the funnel into the same glass flask and aqueous layer was discarded. The rinsate was reduced in volume by rotary evaporation. The concentrated sample was transferred to a conditioned cartridge and eluted with a 90:10 solution of hexane:diethyl ether.

The eluate was evaporated to approximately 1 mL and then brought to 9.0 mL with HPLC grade hexanes. A 1.0 mL aliquot of HPLC grade EtOAc was added to the eluate and the solution was capped and shaken vigorously. An aliquot of the shaken solution was placed in a 2-mL GC vial for GC/MSD analysis.

Each of the ten individual creosote components was quantitated as if it expressed the total amount of creosote in the sample. The normalized residues for each of the individual creosote components were averaged together to represent "total creosote" for that particular dermal sample. The "total" dermal exposure for each replicate for each worker was calculated by summing the normalized residue levels in his WBD arms, WBD top, WBD bottom (torso portion and legs, cut apart at EN-CAS and analyzed as separate samples), and all glove dosimeters worn during that replicate.

Inhalation

The benzene-soluble creosote fractions (coal tar pitch volatiles, or CTPVs) in/on the PTFE air sampling filters were determined using the validated UEC SOP #02-006, dated 3/18/99. The eleven individual creosote components (PNAs) were determined in the XAD-2 resin air sampling tubes using the validated UEC SOP #04-022, dated 10/9/98.

Each PTFE filter was transferred from its cassette to a beaker. Benzene was added to the beaker and the beaker was sonicated for 20 minutes. The extract was decanted through a benzene-rinsed glass-fiber filter in a sintered glass funnel, and vacuum filtered into a concentrator tube. Additional benzene was added to the beaker, swirled, and added to the concentrator tube. Additional benzene was also added to rinse the funnel, and was collected int concentrator tube. The extract was reduced to < 3.0 mL with nitrogen, and made up to 3.0 mL with benzene. The

extract was then drawn into a syringe and used to rinse the sides of the concentrator tube, to recover any creosote on the sides of the tube. One half of the extract was transferred to a pre-weighed cup. The cup was retained in a desiccator overnight, and then re-weighed. The other half of the extract was placed in a vial and capped to be used for the determination of the 11 individual PNAs.

For each XAD-2 resin tube, the plastic cap was removed from the rear end of the tube. The rear glass wool plug was then removed and discarded. The rear-section XAD-2 resin and the middle glass wool plug were transferred to an amber vial and capped. The front-section XAD-2 resin and the front glass-wool plug were transferred to another amber vial and capped. Toluene was added to each vial. The vial was immediately screw-capped, and placed into an ultrasonic bath for 30 to 60 minutes. The PTFE filters subjected to SOP #02-006, described above, were diluted with toluene and sonicated. A portion of each of these sonicated samples was pipetted into an amber glass vial for analysis using an HP GC with a flame ionization detector.

6.0 RESULTS

6.1 Method Validation

6.1.1 EN-CAS Method ENC-2/99 - (determination of creosote in fabrics)

This method was validated by fortifying sets of 7 control WBD sections and glove pairs with reference standard creosote at each of the following concentrations: 60 μg/sample, 6000 μg/sample, 60000 μg/sample, and 0 μg/sample (control). The limit of quantitation (LOQ) for total creosote in cotton WBD fabric samples and glove pairs was 60 μg/sample. The limit of detection was set at 50% the LOQ (30 μg/sample). Recoveries for the control samples were below the LOQ. Table 1 shows a summary of the total creosote recoveries from these fortified samples.

Table 1. Method Validation Results for Total Creosote Detection in Fabrics

Matrix	Fortified Level (μg/sample)	% Recovery of Total Creosote		
		Mean	S.D.	% cv
WBD Sections	60	83 (n=7)	8.9	10.70
	6000	78 (n=7)	3.6	4.62
	60000	75 (n=7)	4.5	6.00
Glove Pairs	60	101 (n=7)	6.8	6.73
	6000	86 (n=7)	7.0	8.14
	60000	85 (n=7)	10.6	12.4

n = number of replicates per fortification level.

6.1.2 UEC SOP #02-006 - (determination of CTPVs in/on PTFE air sampling filters)

This method was validated by fortifying sets of 7 control filters with reference standard creosote (in benzene) at each of the following concentrations: 79 μg/sample, 793 μg/sample, 7930 μg/sample, and 0 μg/sample (control). The LOQ for CTPVs in air sampling filters was 79 μg/sample. The LOD was calculated as 20 μg/sample. Recoveries of benzene-soluble fraction from fortified samples are summarized in Table 2. Recoveries of CTPVs from all control samples were less than the LOQ.

Table 2. Method Validation Recoveries for CTPVs in/on PTFE Air Filters

Fortified Level (μg/sample)	% Recovery of CTPVs		
	Mean	S.D.	% cv
79	116.8 (n=7)	6.40	5.48
793	103.1 (n=7)	3.14	3.05
7930	90.1 (n=7)	1.97	2.18

n = number of replicates per fortification level.

6.1.3 UEC SOP #04-022 - (determination of individual creosote components in XAD-2 resin air sampling tubes and PTFE air sampling filters)

This method was validated for determination of specific target PNAs in XAD-2 resin tubes by fortifying sets of 7 unexposed samples of XAD-2 resin tubes extracted from single sections of unexposed sampling tubes with mixed reference standard PNAs (in toluene) at each of the following concentrations: the LOQ of each compound, 5 times the LOQ of each compound (the highest concentrations that could be prepared without precipitation), and at 0 μg/sample (control). Table 3 summarizes the LODs, LOQs, and method validation percent recoveries for the specific target PNAs in XAD-2 resin tubes. Recoveries from all control samples were below the LOQ.

This method was also validated for determination of specific target PNAs in or on PTFE air sampling filters by fortifying sets of 7 unexposed filters with mixed reference standard PNAs (in toluene) at each of the following concentrations: the LOQ of each compound, 5 times the LOQ of each compound, and 0 μg/sample (control). Table 4 summarizes the LODs, LOQs, and method validation percent recoveries for the specific target PNAs in/on PTFE air sampling filters.

Recoveries of all the control samples were below the LOQ. The results from this method validation demonstrated the adequacy of the method for determining all analytes in/on PTFE air sampling filters at the 5 times the LOQ fortification level. Recoveries of naphthalene, 1- and 2-methylnaphthalenes, dibenzofuran, and to a lesser extent acenaphthene, were unacceptable at the lower (LOQ) fortification level, presumably due to their lower molecular weights and resulting increased volatility. (The other analytes were recovered at acceptable levels from samples spiked at both levels.)

Table 3. Method Validation Recoveries for PNAs in XAD-2 Resin Tubes

PNAs	LOD (μg)	LOQ (μg)	Fortification Levels (μg/sample)	% Recoveries of PNAs		
				Mean	S.D.	% cv
Naphthalene	0.41	20.5	20.5	100.0 (n=7)	0.745	0.742
			102.5	99.0 (n=7)	2.29	2.31
2-Methylnaphthalene	0.47	22.1	22.1	99.8 (n=7)	0.684	0.692
			110.5	98.3 (n=7)	2.15	2.19
1- Methylnaphthalene	0.53	20.1	20.1	100.0 (n=7)	0.882	0.881
			100.5	99.0 (n=7)	2.21	2.23
Acenaphthene	0.47	22.7	22.7	101.0 (n=7)	0.751	0.747
			113.5	99.0 (n=7)	2.12	2.14
Dibenzofuran	0.69	21.2	21.2	97.8 (n=7)	0.977	0.998
			106.0	98.9 (n=7)	2.07	2.09
Fluorene	0.48	20.9	20.9	99.7 (n=7)	0.716	0.718
			104.5	98.2 (n=7)	2.10	2.14
Phenanthrene	0.36	21.0	21.0	100.0 (n=7)	0.530	0.529
			104.5	99.4 (n=7)	2.05	2.06
Anthracene	0.51	20.0	19.2	99.8 (n=7)	0.895	0.897
			96.0	98.9 (n=7)	2.04	2.07
Pyrene	0.47	21.0	21.0	101.0 (n=7)	0.673	0.664
			105.0	99.1 (n=7)	1.86	1.88
Chrysene	0.36	23.4	19.1	101.0 (n=7)	0.676	0.672
			95.5	99.3 (n=7)	1.90	1.91
Benzo(a)pyrene	0.51	25.8	25.8	102.0 (n=7)	0.687	0.676
			129.0	99.2 (n=7)	1.97	1.99

n = number of replicates per fortification level.

Table 4. Method Validation Recoveries for PNAs in/on PTFE Air Filters

PNAs	LOD (μg)	LOQ (μg)	Fortification Levels (μg/sample)	% Recoveries of PNAs		
				Mean	S.D.	% cv
Naphthalene	0.41	20.5	20.5	2.58 (n=7)	6.82	265
			103	0.7 (n=7)	15.90	2.98
2-Methylnaphthalene	0.47	22.1	22.1	28.4 (n=7)	10.0	35.4
			111	2.7 (n=7)	9.75	3.31
1- Methylnaphthalene	0.53	20.1	20.1	24.8 (n=7)	12.0	48.4
			101	3.1 (n=7)	12.03	3.54
Acenaphthene	0.47	22.7	22.7	62.4 (n=7)	6.17	9.88
			114	61.9 (n=7)	2.27	3.67
Dibenzofuran	0.69	21.2	21.2	72.1 (n=7)	3.06	4.25
			106	70.8 (n=7)	2.04	2.88
Fluorene	0.48	20.9	20.9	79.6 (n=7)	2.47	3.10
			105	79.5 (n=7)	2.70	3.39
Phenanthrene	0.36	21.0	21.0	90.2 (n=7)	2.95	3.27
			105	88.8 (n=7)	2.80	3.16
Anthracene	0.51	20.0	19.2	89.5 (n=7)	3.42	3.82
			96	90.4 (n=7)	2.78	3.08
Pyrene	0.47	21.0	21.0	98.0 (n=7)	3.71	3.79
			105	95.1 (n=7)	2.83	2.98
Chrysene	0.36	23.4	21	93.3 (n=7)	4.48	4.80
			105	92.6 (n=7)	3.07	3.31
Benzo(a)pyrene	0.51	25.8	25.8	89.3 (n=7)	2.64	2.95
			129	91.5 (n=7)	3.24	3.54

n = number of replicates per fortification level.

These results demonstrated that the proposed combination of filter and resin tube filter train would be necessary for adequate retention of all selected analytes during field sampling.

6.2 Breakthrough/Retention Testing

Breakthrough/retention testing was performed in order to insure that creosote components would not migrate from the XAD-2 resin particles. All of the control recoveries of all analytes were below the LOD for this test. At the LOQ spike level, all of the analytes were retained in the filters or front tubes. Very low levels of naphthalene were found in one of the high-level spiked rear tube but no other creosote component was detected. This naphthalene recovery was thought to possibly be due to contamination during handling in the analytical laboratory.

6.3 Pre-field Recovery of Creosote in Dermal Matrices

A pre-field recovery study of creosote in dermal matrices was performed in order to determine that creosote applied to glove dosimeters and WBD fabric would be retained by those matrices during field sampling and transport. The mean percent recoveries showed some loss of creosote compontents on full-day exposure to ambient conditions. However, according to the Study Report, the results were within the range generally considered acceptable for field samples. The average recovery for the WBDs exposed to ambient conditions for 8 hours was 69.2% $\pm$ 9.1%. The average recovery for the WBDs which were spiked but not exposed to ambient conditions was 87.6% $\pm$ 10.3%. The average recovery for the gloves exposed to ambient conditions for 8 hours was 63.4% $\pm$ 9.4%. The average recovery for the gloves which were spiked but not exposed to ambient conditions was 85% $\pm$ 3.23%.

6.4 Laboratory Spikes

Laboratory fortified samples of each matrix used in the study were analyzed concurrently with field samples to monitor procedural recoveries. The mean recovery of total creosote from laboratory fortified glove and WBD samples is summarized in Table 5. The mean recoveries of total creosote ranged from 85.4% to 89.3%. These recoveries were well within the acceptable range.

Table 5. Recovery of Total Creosote from Laboratory Fortified Dermal Matrices

Matrix	Mean %	S.D.	No. of Reps.
Glove (2)	89.1	11.7	69
Whole Body Dosimeter (WBD):			
arm(2)	89.3	7.47	28
top	85.4	8.08	30
brief	88.2	7.03	24
leg (2)	86.0	7.09	24

The mean recoveries of creosote components from laboratory fortified XAD-2 resin tubes are summarized in Table 6. The laboratory fortification levels were at the LOQ and 5 times the LOQ for each component. The mean recoveries at the LOQ level ranged from 76 to 98.7%. The mean recoveries at 5 times the LOQ level ranged from 72.7 to 87%. The overall mean recoveries for both fortification levels ranged from 74.3 to 92.8%. All of the mean recoveries for the creosote components are within the acceptable range. Chrysene had the lowest recovery at both fortification levels.

The mean recovery from 12 samples fortified in the laboratory at 10 times the LOQ (0.790 mg) of CTPVs in PTFE air sampling filters was 84.0 $\pm$ 7.3%. According to the registrant, the results from all of these laboratory fortified recoveries agree favorably with the method validation recoveries.

6.5 Field Spikes

Field fortification samples were prepared once at each facility. Unexposed WBD sections, paired glove dosimeters, single air sampling filters, and complete air sampling trains were fortified in the field to assess potential degradation or reduced extractability of residues due to exposure to environmental conditions, handling, packaging, shipping, and frozen storage.

Dermal Field Fortification Samples

Field fortified sets of 3control WBD sections and glove pairs with reference standard creosote were prepared at each site at each of the following concentrations: 60 μg/sample, 60000 μg/sample, and 0 μg/sample (control). Results from dermal field fortification samples are presented below in Table 7. Overall field fortification recoveries at Site A for whole body dosimeters (WBD's) and gloves were 68 and 78%, respectively. Overall field fortification recoveries at Site B for whole body dosimeters (WBD's) and gloves were 96 and 62 %, respectively. Overall field fortification recoveries at Site C for whole body dosimeters (WBD's) and gloves were 72 and 69 %, respectively. Overall field fortification recoveries at Site D for whole body dosimeters (WBD's) and gloves were 71 and 66 %, respectively. There were however some fortification levels which yielded extremely high recoveries for WBD's and some low recoveries for gloves. For example, at a 60 µg/sample "total creosote" fortification for Site B, there were recoveries for the WBD's as high as 150% and recoveries for the gloves as low as 52.3%. There were measurable amounts of total creosote found in each of the control samples prepared at each facility. The field fortification values were corrected based on these control samples. Therefore, the field fortification recovery value is minus the amount of total creosote found in the control samples.

Table 6. Recovery of PNAs from Laboratory Fortified XAD-2 Resin Tubes

Fortification level		% Recoveries of: *										
		N	**2-MN**	**1-MN**	**AC**	**DBF**	**F**	**PH**	**AN**	**PY**	**CH**	**BAP**
LOQ	Mean (n=22)	89.3	86.1	86.0	86.0	98.7	84.0	81.0	82.0	85.0	76.0	81.9
	SD	21.1	20.5	20.4	20.1	33.3	20.5	19.8	19.7	18.5	16.4	20.0
5 x LOQ	Mean (n=22)	83.8	82.6	82.4	82.2	87.0	80.4	72.9	80.5	77.4	72.7	75.9
	SD	25.4	25.2	25.5	25.9	25.4	25.1	25.7	26.2	25.2	24.5	24.6
Overall Mean Recovery		86.5	84.3	84.2	84.1	92.8	82.2	76.9	81.2	81.2	74.3	78.9

* N= naphthalene; 2-MN = 2-methylnaphthalene; 1-MN = 1-methylnaphthalene; AC= acenaphthene; DBF = dibenzofuran; F = fluorene; PH = phenanthrene; AN = anthracene; PY = pyrene; CH = chrysene; and BAP = Benzo(a)pyrene.
(n)= number of replicates

Table 7. Field Fortification Recoveries for Total Creosote Detection in Fabrics

Matrix	Fortified Level (μg/sample)	% Recovery of Total Creosote		
		Mean	S.D.	Overall
Site A				
WBD Sections	60	65.8	1.7	67.6 (n=6)
	60000	69.4	1.0	
Glove Pairs	60	68.7	11.1	78.4 (n=6)
	60000	88.2	1.1	
Site B				
WBD Sections	60	122	24.3	96.3 (n=6)
	60000	70.6	2.8	
Glove Pairs	60	54.5	2.6	62.4 (n=6)
	60000	70.4	1.9	
Site C				
WBD Sections	60	66.8	4.0	71.8 (n=6)
	60000	76.9	3.9	
Glove Pairs	60	63.8	10.5	69.1 (n=6)
	60000	74.4	6.1	
Site D				
WBD Sections	60	74.3	5.8	71.5 (n=6)
	60000	68.8	6.5	
Glove Pairs	60	61.1	11.0	66.5 (n=6)
	60000	72.0	5.5	

Inhalation Field Fortification Samples

At Sites B through D, triplicate XAD-2 resin tubes were fortified with a solution of mixed PNAs (in toluene) at 0 ppm (control), the LOQ of each compound, and 5 times the LOQ of each compound. Each sampling tube was connected to a Buck S.S. pump that then ran for 8 hours at

approximately 1 L/minute. Results from inhalation field fortification XAD-2 resin-filled sampling tubes are presented below in Table 8. Overall field fortification recoveries for all of the polynuclear aromatic hydrocarbons (PNAs) ranged from 78 to 180% at Site B, from 62 to 96% at Site C, and from 69 to 124% at Site D. At Site B, the high recovery was for dibenzofuran. At Site C, the lowest recoveries were for fluorene and phenanthrene. At Site D, the high recoveries were for chrysene.

Additional triplicate sampling trains, each consisting of two air sampling filters in in-line cassettes, were spiked with a solution of standard creosote (in benzene) at 0 ppm, the LOQ, or 10 times the LOQ. Each train was connected to a Buck S.S. pump that then ran for 8 hours at approximately 1.0 L/minute. Results from these field fortification recoveries for CTPV in/on the PTFE filters which were attached to sampling tubes are presented in Table 9. The Overall percent recoveries for the coal tar pitch volatiles (CTPVs) were poor. The overall recovery for Site B was 57%. The overall recoveries for Sites C and D were 51 and 57%, respectively. The registrant did not address these poor inhalation field fortification results.

6.6 Formulation Testing

The field phase of this study was performed using commercial wood treatment systems that could not economically be shut down, solvent-cleaned, and filled with analyzed lots of test substances for this study. Instead, study personnel collected 100 to 200 mL sample aliquots of the mixed application solutions which were used during the monitored work cycles, and shipped them to EN-CAS for later analysis. Study personnel and/or test site personnel collected at least one sample of the on-site product used to treat lumber products during monitoring at each site. Four such samples were subjected to GLP-compliant compositional analysis (results were provided in the study raw data). The creosote used at each test site was analyzed by the producer for compliance with AWPA specifications, and was determined to be within those specifications, as noted on the certificates of analysis supplied with the creosote.

The Koppers Creosote Solution (“P2") used for application to railroad ties as Sites A, C, and D had a purity of nominally 95% AWPA P2 creosote. The Koppers Coal Tar Creosote (“P1") used at Site C for application to utility poles had a purity of nominally 98.5% AWPA P1/P13 creosote. The Coal Tar Creosote (P-1/P13) Wood Preservative used for application to wood at Site B had a purity of nominally 100% P1/P13 creosote.

Table 8. Field Fortification Recoveries for PNAs in XAD-2 Resin Tubes

	Fortification level	% Recoveries of: *										
		N	**2-MN**	**1-MN**	**AC**	**DBF**	**F**	**PH**	**AN**	**PY**	**CH**	**BAP**
Site B												
Average Recovery	LOQ (n=3)	104	94.9	100	87.3	221.8	74.1	73	81.1	89.4	91	96.1
	5 x LOQ (n=3)	130	122	126	112	139	88.3	83.9	74.5	80.4	83.7	88.2
Overall Recovery		117	109	113	100	180	81	78	78	85	87	92
S.D.		42.8	39.3	40.7	35.1	60.9	21.1	10.8	6.0	7.0	5.8	6.7
Site C												
Average Recovery	LOQ (n=3)	97.7	83.6	82.2	69.5	67.5	58.3	59.2	71.6	79.2	93.5	101
	5 x LOQ (n=3)	90.1	81.9	81.4	72.1	70.4	65.3	68.5	80.0	80.8	86.2	91
Overall Recovery		94	83	82	71	69	62	64	76	80	90	96
S.D.		8.1	5.1	5.3	5.6	5.3	5.8	7.0	7.2	5.8	5.7	7.9
Site D												
Average Recovery	LOQ (n=3)	74.6	85.6	82.4	79.3	78.1	72.7	61.4	68.7	77.5	123	107
	5 x LOQ (n=3)	106	102	100	92.6	87.6	82.7	76.8	84.9	84.4	126	110
Overall Recovery		91	94	91	86	83	78	69	77	81	124	109
S.D.		22.6	18.7	18.5	17.9	16.8	15.8	15.1	11.6	7.4	2.9	2.6

* N= naphthalene; 2-MN = 2-methylnaphthalene; 1-MN = 1-methylnaphthalene; AC= acenaphthene; DBF = dibenzofuran; F = fluorene; PH = phenanthrene; AN = anthracene; PY = pyrene; CH = chrysene; and BAP = Benzo(a)pyrene.

Table 9. Field Fortification Recoveries for CTPV in/on PTFE Filters Attached to Air Sampling Tubes

Test Site	Fortification Level	Average Recovery (%)	S.D.	Overall Recovery (%)
B	LOQ	52.3 (n=3)	8.2	57
	10 x LOQ	61.5 (n=3)	1.7	
C	LOQ	51 (n=3)	3.9	51
	10 x LOQ	50.9 (n=3)	0.9	
D	LOQ	52.3 (n=3)	8.2	57
	10 x LOQ	61.5 (n=3)	1.7	

6.7 Storage Stability

Dermal

The stability of total creosote was determined in WBD sections (arm pairs) and pairs of glove dosimeters stored frozen after fortification with 3,000 μg/sample (50 times the LOQ). Five sets of WBD sections and glove pairs were stored frozen by EN-CAS for up to 329 days, respectively, at $\leq$ -11.1 ^{o}C prior to residue extraction at the following storage intervals: 0, 10, 30, 90, and 329 days. Each set consisted of one control, 2 WBD sections and glove pairs exposed at the time of setup, and 2 WBD sections and glove pairs exposed just prior to residue extraction. The mean creosote recoveries for the WBD sections and glove pairs ranged from 87.6 to 97.4% through out the stability study period (0 to 329 days). Mean creosote levels in WBD samples and glove pairs stored at $\leq$ -11.1 ^{o}C for 90 and 329 days declined by approximately 5% and approximately 10%, respectively. WBD and glove pair samples collected from the field were stored frozen at EN-CAS for up to 161 days and 92 days, respectively, at $\leq$ -11.1 ^{o}C prior to residue extraction. According to the registrant, the results from the dermal media storage stability study demonstrate the stability of creosote residues in frozen dermal exposure monitoring media.

Inhalation

The stability of creosote components was determined in XAD-2 resin tubes and PTFE air sampling filters stored frozen after fortification with 5 times the LOQ of each component. Five sets of resin tubes and air filters were stored frozen by UEC for up to 60 days, at $\leq$ -17 ^{o}C, prior to residue extraction at the following storage intervals: 0, 10, 30, and 60 days. Each set consisted of one control, 2 resin tubes (or 2 air filters) exposed at the time of setup, and 2 resin

tubes (or 2 air filters) exposed just prior to residue extraction.

The average percent recoveries for the individual creosote components in the XAD-2 resin tubes ranged from 92.1 to 98.5% after 30 days of frozen storage. The average percent recoveries for the individual PNAs ranged from 79.3 to 86.6% after 60 days of frozen storage. The average percent recovery of each of the PNAs in the XAD-2 resin tubes showed that PNA levels in XAD-2 resin declined < 10% after 30 days, and (with the exception of benzo(a)pyrene) , 20% after 60 days of frozen storage. Values for worker samples stored over 30 days were corrected for the results of this test.

The average percent recoveries for the individual PNAs in the PTFE air filters ranged from 0.0 to 145% after 30 days of frozen storage. After 60 days of frozen storage, the average percent recoveries for the individual PNAs ranged from 2.4 to 142%. On the PTFE air sampling filters, anthracene, pyrene, chrysene, and benzo(a)pyrene showed no decline over 60 days. Phenanthrene declined by < 10% over 60 days. The lighter molecular weight PNAs declined markedly during frozen storage; however, because the air filters used were expected to pass volatile PNAs during exposure, and because PNAs were not present at $\geq$ LOQ in any samples collected, worker sample values were not corrected for these results.

In preliminary testing, reference standard creosote was applied to PTFE air sampling filters at 3 times the LOQ and 5 times the LOQ. After 15, 30, and 60 days of storage at $\leq$ -17 ^{o}C, recoveries of CTPVs from fortified filters were 75.1%, 75.8%, and 66.1%, respectively, of the original fortification level. Again, because CTPVs were $\geq$ LOQ in only two samples collected, worker sample values were not corrected for these results.

XAD-2 resin tubes and PTFE air filters collected in the field were stored frozen by UEC for up to 51 days, at $\leq$ -17 ^{o}C, prior to residue extraction.

6.8 Exposures

Known quantities of a characterized creosote formulation was not measurable for this study because the study was set up in a continuously operating commercial setting. The creosote was applied in closed systems which recovered and retained excess treatment solution from the wood and treatment vessels while sealed. Therefore, the amount of product or active ingredient handled by each worker is not known. According to the study, the major source of creosote for worker exposure in these types of facilities is preservative remaining on or escaping from treated wood or equipment that had been in a cylinder during treatment. This is presumably a very small fraction of the quantity actually applied to and retained by the charge. The mean pounds of creosote retained per charge per site are as follows:

Site A	19004 lbs
Site B	11289 lbs
Site C	25999 lbs
Site D	25978 lbs

Sites A and B had shortened monitoring periods due to weather and maintenance related facility closures. Differences among Sites B, C, and D in the amount of creosote applied per charge were largely due to differences in the available cylinder volume at each site.

Dermal Results

Dermal worker exposure was measured for each of the workers' tasks identified in section 3.1. During each replicate of monitoring, exposure of the subject's body (excluding that of the face, neck, and hands) to creosote components was determined by collection of material in/on his cotton WBD. Exposure of his hands was determined from material collected in/on his cotton glove dosimeters (worn under his chemical-resistant gloves if appropriate).

The unadjusted creosote level for each WBD segment and glove pair from each worker was corrected for the mean recovery of the appropriate analytical standard(s) from samples of the appropriate matrix fortified in the field at that test site. The analytical method was subject to some variability at levels near the LOQ, suggesting that recoveries obtained at that level were likely to be less reliable than those at the higher level. Therefore, the field fortification recoveries at 1,000 times the LOQ were used to make the adjustment. The registrant did not make any adjustments when field fortification recoveries were > 100%. U.S. EPA guidelines state that corrections are not needed when field fortification recoveries are above 90%. For any sample in which the "total creosote" level was below the LOQ but above the LOD, ½ the LOQ was used as an upper-bound estimate of the residue in the sample for calculation of calculated exposure. In addition, for any sample in which the "total creosote" level was below the LOD, ½ the LOD was used as the upper-bound estimate for calculation. The use of ½ LOD and ½ LOQ values was the same for the inhalation data.

Each calculated exposure level was normalized to μg/kg worker body weight/day, normalizing results to the U.S. EPA's recommended mean adult weight of 71.8 kg and to a standard work day length of 8 hours. The "total" dermal exposure for each replicate for each worker was calculated by summing the normalized residue levels in his WBD arms, WBD top, WBD bottom (torso portion and legs, cut apart at EN-CAS and analyzed as separate samples), and all glove dosimeters worn during that replicate.

The levels of total creosote found in workers' gloves and WBDs (combined) are shown in Tables XIX, XX, XX1, and XXII (pages 126 through 140) in the Study Report. The calculated geometric mean daily dermal exposure levels of monitored workers at all sites are summarized in Table 10, below. Geometric mean dermal exposures across all of the job functions at all four sites ranged from 25 (Load-Out Area Helper) to 901 (Oil Unloader) μg/kg bw/day. The highest individual levels were found in the Site C TO, who was also performing the duties of the OU while not wearing chemical-resistant gloves on at least one monitored occasion. Within each job class monitored, and over all classes at each site, those individuals whose activities involved the greatest proximity to creosote sources were exposed to the highest levels of creosote.

Differences in exposures were pronounced from site to site, with the smallest exposure

levels observed at Site B, which applied the smallest amount of creosote, and which included an air-handling system to remove creosote vapors from the cylinder door area. The highest exposures were found at Site C, which was the site which used the second-highest quantity of creosote and where the CHs regularly contacted and handled freshly treated ties.

Table 10. Geometric Mean Daily Dermal Exposure Levels of Monitored Workers at all Sites

Parameter	Dermal Exposure (μg/kg bw/day) to Creosote of : *											
	TO	**TA**	**TB**	**WO**	**OU**	**CLO**	**CH**	**LLO**	**LLO (F)**	**LH**	**DP**	**CK**
# Replicates	18	4	9	8	9	18	10	14	5	4	4	5
Minimum	15.1	20.8	94.9	27.1	349.4	45.9	40.1	14.1	102.4	18.8	213.2	269.1
Maximum	49573	33	3118	377	2560	3987	3446	591	771	37	395	2341
Mean	5051	27	759	170	1203	773	1190	119	278	26	280	877
S.D.	12877	6	1005	152	943	1115	1075	149	278	8	86	850
G.M.	360	27	385	108	901	313	626	69	208	25	271	638
Median	369	28	365	107	680	191	1213	60	169	25	257	586

*Abbreviations: CH = cylinder area loader helper; CK = checker; CLO = cylinder area loader operator; DP = drip pad labor; LLO = load-out area loader operator; LLO(F) = load-out area forklift operator; OU = oil unloader; TA = treating assistant; TB = test borer; TO = treating operator; WO = water treatment system operator; LH = load-out area loader helper.

Inhalation Results

Inhalation to monitored workers was measured for each of the tasks identified in section 3.1 at Sites B, C, and D. No useful inhalation data were generated at Site A due to problems with the air sampling methodology. The methodology was changed prior to sampling at Sites B, C, and D. The unadjusted residue level for each air sampler from each worker was corrected for the mean recovery of the appropriate analytical standard(s) from samples of the appropriate matrix fortified in the field at that test site. Inhalation exposure for each target compound was calculated from material found in the entire sampling train (filter + front tube + rear tube). Calculated inhalation exposure levels were normalized by scaling up the pump flow rate of 1 L/minute to the U.S. EPA's recommended minute ventilation rate of approximately 18.34 L/minute for "light activities". Then an adjustment was made for the standard EPA-recommended adult weight of 71.8 kg. According to the Study Report, due to the fact that none of the workers monitored in this study performed continuous light activity, the use of the recommended ventilation rate probably resulted in a notable over estimation of exposure. The fact that values were generated even for those compounds that were never detected or quantifiable in field samples contributes to the over estimation of inhalation exposures as well.

No air samplers showed quantifiable levels of most of the PNAs monitored. Chrysene and benzo(a)pyrene was not detected in worker samplers. Pyrene and anthracene were detected in 1 and 2 samples, respectively. However, naphthalene was detected by every sampler, and 2-methylnaphthalene was detected in most samplers, suggesting that only the lower molecular weight ("low-boiling") PNAs are commonly volatilized during pressure treatment, or are able to remain volatile when exposed to ambient temperatures. These results suggest that the highest molecular weight PNAs did not volatilized during the treatment process, and may have continued to be emitted from treated materials during cooling, increasing their availability for worker exposure. Naphthalene was the single greatest contributor to inhalation exposure measurement. CTPVs were present at quantifiable levels in only one sampler, suggesting that this class of compounds may be a minor constituent of creosote emissions. Measured aerial concentrations of naphthalene (approximately 0.04 to 1.29 mg/m^3) and CTPVs (0.0003 to 0.0006 mg/m^3) were well below the ACHIH TLVs of 52 mg/m^3 and 0.2 mg/m^3, respectively, for these materials for all monitored workers. As noted for dermal exposure, geometric mean daily inhalation exposure was greatest in those worker classes who performed those tasks most likely to put them in close proximity to sources of creosote.

The calculated levels of inhalation exposure to creosote components by monitored workers at each site are presented in Tables XXVI, XXVII, and XXVIII (pages 144 through 146) in the Study Report. The levels of each analyte in the air sampled during each monitored work cycle, expressed as $\mu g/m^3$ of air, are presented in Table XXIX (pages 147 to 149) in the Study Report.

7.0 REVIEW OF THE STUDIES COMPLIANCE WITH SERIES 875

Compliance with Series 875- Occupational and Residential Exposure Test Guidelines of the Pesticide Assessment Guidelines (U.S. EPA, 1998) is critical if a study is to be considered acceptable to the Agency. Table 11 is based on the "Checklist for Applicator Monitoring Data" used by the U.S. EPA/OPP/HED in reviewing Series studies. This table is designed to summarize Series 875 guidelines, identify whether the study addresses these issues, and is compliant with these guidelines and it also present comments on how to bring the study into compliance.

8.0 SUMMARY OF DATA GAPS WITH RESPECT TO SERIES 875

Pertinent items with regard to scientific validity and Series 875 compliance, not addressed above, are discussed below. The following issues were noted:

- The amount of product applied and the amount of active ingredient handled by each worker was not calculated because the creosote was applied in a closed system which recovered and retained excess treatment solution from the wood and treatment vessel while sealed.

- The number of field fortification samples collected at the sites were not enough to satisfy the Series 875 guidelines. According to the guidelines, there should have been field at least one fortification sample per worker per monitoring period (8 hour shift) per fortification level (three levels) for each matrix and at least one field blank per worker per monitoring period for each matrix. There were more workers monitored than there were field fortification and field blank samples collected.

- There were some dermal fortification levels which yielded extremely high recoveries for WBD's and some with unacceptably low recoveries for gloves. For example, at a 60 µg/sample "total creosote" fortification for Site B, there were recoveries for the WBD's as high as 150% and recoveries for the gloves as low as 52.3%. There were measurable amounts of total creosote found in each of the control samples prepared at each facility. All dermal fortification recoveries above 120% and below 70% should be considered unacceptable according to Series 875 guidelines and undermine the validity of the results.

- The inhalation exposure data was summarized in the form of bar graphs in the Study Report. However, data points used for the graphs were not provided. The raw data was provided but the raw data tables did not reflect the data presented in the bar graphs. Therefore, it was difficult to validate the conclusions made in Study Report.

- The Overall inhalation field fortification percent recoveries for the coal tar pitch volatiles (CTPVS) were poor. The overall recovery for Site B was 57%. The overall recoveries for Sites C and D were 51% and 57%, respectively. All inhalation fortification recoveries below 70% should be considered unacceptable according to Series 875 guidelines and undermine the validity of the results.

Table 11. Compliance with Series 875

FIFRA Compliance Checklist	Does the study address this compliance issue?	Does the study comply with this part of Series 875?	Comments
Prior "informed consent" must be obtained in writing from all subjects who will be exposed in the study.	yes	yes	Informed consent was obtained in writing from each of the workers monitored in the study.
All conditions specified on the product label must be observed, including whatever protective clothing is specified for workers to wear.	yes	mostly	Each worker was supplied with protective clothing, gloves, respirators as needed. However, according to the study, not all workers wore the proper protective gloves while working.
Studies must be designed so that an exposure is measured separately for each activity associated with an application.	yes	yes	10 job categories were monitored.
Data collection in accordance with 40 CFR 160, Good Laboratory Practice Standards.	yes	partly	The creosote used at each test site was analyzed for compliance with AWPA specifications, and these analyses were not performed per FIFRA GLPs. Characterization of reference standards were not done per FIFRA GLPs. GLP-compliant calibration of creosote storage and application equipment was not configured. Corrections to field data were not done per FIFRA GLPs.
Typical end use product of the active ingredient used.	yes	yes	The study identifies 3 end use products used in this study. They are Koppers Coal Tar Creosote (P1/P13), VFT Coal Tar Creosote (P1/P13) Wood Preservative, and Koppers Creosote Solution. Labels for all three end use products were provided.
End use product handled and applied using recommend equipment, application rates, and typical work practices.	yes	yes	Typical wood treatment process assessed.

Table 11: Compliance with Series 875 (Continued)

FIFRA Compliance Checklist	Does the study address this compliance issue?	Does the study comply with this part of Series 875?	Comments
For exposure monitoring at least five replicates (e.g, individuals) at each of at least three sites for each job function should be monitored.	yes	mostly	There were 25 workers total (for all four sites) monitored for up to 4 - 5 consecutive work days. There were 10 job categories monitored. For each job category there were 4 to 19 replicates per site.
Monitoring period is sufficient to collect measurable residues but not excessive so that residue loss occurs.	yes	yes	Exposure periods seemed long enough for the tasks required.
Dermal and/or inhalation exposure must be monitored by validated methodologies. Biological monitoring is consistent with and supported by pharmacokinetic data accepted by the Agency.	yes	yes	Dermal and inhalation methods used were identified in Series 875 regulations.
Quantity of active ingredient handled and duration of monitoring period reported for each replication	no	partly	Quantity of active ingredient handled was not described. Duration of exposure was identified for both dermal and inhalation exposures.
Quantitation level of detection is at least 1 $\mu g/cm^2$	not applicable	not applicable	Since whole body dosimeters and inhalation samples were used this is not applicable. This LOQ is used only for dermal patch studies.
Clothing worn by each study participant and location of dosimeters reported.	yes	yes	Study used whole body dosimeters (cotton thermal shirts, pants, and gloves). Sections (gloves, arms, bottoms) were measured appropriately.
Storage of samples consistent with storage stability data.	yes	yes	Storage of samples and storage stability are addressed in the study and samples were corrected when appropriate according to storage stability results.

Table 11: Compliance with Series 875 (Continued)

FIFRA Compliance Checklist	Does the study address this compliance issue?	Does the study comply with this part of Series 875?	Comments
Efficiency of extraction in laboratory provided as mean plus or minus one standard deviation. Lower 95 percent confidence limit is not less than 70 percent based on a minimum of seven replications per fortification level or prior Agency approval of extraction methodology provided.	yes	yes	Method validation testing appeared to be in the acceptable range.
At least one field fortification sample per worker per monitoring period per fortification level for each matrix. At least one field blank per worker per monitoring period for each matrix.	no	no	This study did not provide for at least one field fortification sample per worker monitored per fortification level for each matrix. There were only three fortification samples per fortification level. The field fortification samples were only prepared once.
When collecting urine for biological monitoring, collection should involve 24 hour urine samples. A minimum of one baseline, pre-exposure 24 hour sample must be collected. Twenty-four hour samples must be collected for the day of application and for sufficient days postapplication as determined by the excretion profile of the pesticide.	not applicable	not applicable	

9.0 REFERENCES

1. U.S. Environmental Protection Agency, 1995. *Occupational and Residential Exposure Test Guidelines. OPPTS 875.1100 Dermal Exposure- Outdoor.* Washington DC. May 1995. EPA 712-C-95-262.

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4. "The Chemistry, Toxicity, and Biodegradation of Creosote", 1998. http://inweh1.uwaterloo.ca/biol447new/assignments/creosote.html.

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7. James, J.W., 1996. "Method Validation Study for the Determination of Creosote Residue on Cotton Undergarments," EN-CAS Project 96-0074, for the Creosote Council II, November, 1996.